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**Citation style:** Kansy Jerzy, Hanc Aneta, Giebel Dawid. (2010). The Influence of Heat Treatment on Point Defect Concentration in Fe-Al and Fe-Al-Cr systems. "Nukleonika" (Vol. 55, no. 1 (2010), s. 21-25).



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# The influence of heat treatment on point defect concentration in Fe-Al and Fe-Al-Cr systems

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**Abstract.** FeAl alloys of nominal Al content 28, 38 and 45 at.% and Fe<sub>28</sub>Al<sub>5</sub>Cr with minor alloying elements added to improve their application properties are studied by positron annihilation lifetime analysis. The lifetime spectra of samples FeXAl with  $X \geq 38$  (both quenched and cooled with furnace) are described by a single lifetime component related to the saturated positron trapping by quenched-in vacancies of concentration much higher than 100 ppm. A very strong dependence of retained vacancy concentration on the rate of cooling is shown for Fe<sub>28</sub>Al and Fe<sub>28</sub>Al<sub>5</sub>Cr alloys. After quenching, the concentration is of the order of  $10^{-4}$  whereas in samples slowly cooled it is reduced to  $10^{-5}$ . The chromium addition to Fe<sub>28</sub>Al<sub>5</sub>Cr dismisses the vacancies concentration in comparison to the concentration in Fe<sub>28</sub>Al after the same heat treatment.

**Key words:** positron annihilation • Fe-Al • Fe-Al-Cr • point defects

## Introduction

The intermetallic alloys basing on iron-aluminum ordered phases are characterized by low specific weight, high strength, low cost and good potential for industrial applications as a replacement for high-temperature oxidation resisting or corrosion resisting stainless steel [4]. On the other hand, the lack of ductility at room temperature and a decrease in strength of above 873 K limits the scope of their application as a construction material. However, the addition of alloying elements such as Cr can improve the room temperature ductility of Fe<sub>3</sub>Al [2].

The intermetallic materials from the Fe-Al system with the content of iron larger than 50% have two types of ordering structure, D0<sub>3</sub> structure below 550°C and B2 structure at temperatures between 550°C and 1250°C. The phases are based on the body-centred cubic (bcc) lattice and can exist in a wide range of compositions. The B2 entirely ordered phase relates to stoichiometric FeAl. The B2 structure can undergo ordering of second nearest neighbours to form a complex cubic D0<sub>3</sub> phase when the aluminium content ranges between 25 and approximately 37 at.%. This phase is based on a Fe<sub>3</sub>Al stoichiometry [8].

It is well established that physical and mechanical properties of Fe-Al alloys are related to the atomic ordering and the presence of point defects. As in most ordered materials, the defect structure in the B2 and D0<sub>3</sub> phases is substantially more complicated than in pure metals [4]. Besides single vacancies, one must

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Received: 24 June 2009

Accepted: 15 September 2009

also consider antisite atoms, divacancies, triple defects (combinations of two vacancies on one sub-lattice site with an antisite atom in the other sub-lattice) or any combination of them. Most probably, the predominant type of defect in these materials depends on the intrinsic structures, A2, B2 and D0<sub>3</sub>. During annealing at high temperature, very high concentrations of vacancies form easily in B2 structured Fe-Al alloys which are largely retained in the lattice, even when the alloys are cooled to room temperature at low cooling rates [4]. A large amount of work has focused on the effect of these vacancies on hardness and yield stress, showing that the significant increase of both properties occurs in specimens quenched or air cooled from temperatures above 800°C. Although this hardening effect has been found for all compositions, it becomes more significant when the aluminium content is increased [10].

The aim of this work is to characterize the concentrations and the nature of defects present in FeAl and FeAlCr alloys with minor alloying elements added to improve their application properties. For this purpose, the positron lifetime spectroscopy is employed. Among all the experimental techniques used for the defect structure studies, the positron annihilation spectroscopy has been widely used because of its high sensitivity to the presence of vacancy-type defects.

## Experimental

The materials investigated were multicomponent alloys on Fe-Al basis, the nominal compositions of which are presented in Table 1. Some microadditions were used to improve the high temperature resistance of the alloys and to decrease the grain sizes during the crystallization process. The addition of Cr in the amount of 5 at.% was to increase plastic properties of the alloys. The alloys were produced by vacuum induction melting. The melted material was drop cast into cylindrical graphitoid moulds with a diameter of 12 mm. The surface of so produced rods was cleaned and then the material was broken up and melted again. The procedure was repeated twice. The material was examined in the following states:

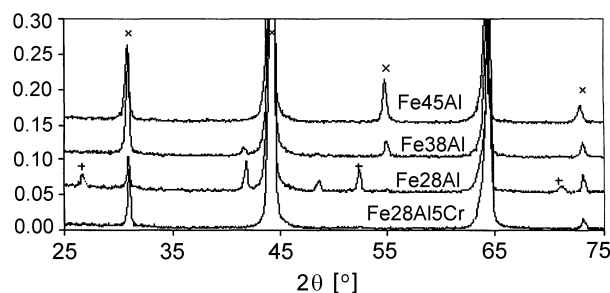
- 1) as-cast,
- 2) homogenized in a chamber furnace at 1000°C for 48 h in air, and then
- 3) slowly cooled with furnace (fur.-C),
- 4) quenched into air (air-Q),
- 5) quenched into oil (oil-Q).

From so prepared rods 2 mm thick samples were obtained by electro-spark cutting.

The X-ray diffraction analysis indicated the presence of D0<sub>3</sub> structure in all investigated Fe28Al samples both after furnace cooling and after oil/air quenching.

**Table 1.** The nominal composition of investigated samples in at. %

Sample	Fe	Al	Cr	Mo	Zr	C	B
Fe28Al	71.64	28.00	–				
Fe28Al5Cr	66.64	28.00	5.00	0.20	0.05	0.10	0.01
Fe38Al	61.64	38.00	–				
Fe45Al	54.64	45.00	–				



**Fig. 1.** The XRD patterns measured for the investigated samples of different compositions after furnace cooling. The 'x' peaks relate to B2 structure, the '+' peaks refer to D0<sub>3</sub> structure. The unmarked peaks in Fe28Al are identified to be Fe<sub>3</sub>AlC<sub>x</sub> reflections. The intensities of peaks are normalized to the intensity of the highest peak in each pattern. For the sake of clarity, the subsequent patterns are shifted by 0.05.

However, in Fe28Al5Cr, independently of their heat treatment, only the ordered B2 phase was found. The ordered B2 structure was also observed in all the samples of higher Al content. In Fig. 1 some selected XRD diffraction patterns are presented for samples of various compositions after furnace cooling.

The positron lifetime measurements were made at room temperature with a conventional fast-fast spectrometer of 270 ps time resolution. The positron source with the activity of about 370 kBq, covered with a 5 μm Ni foil, was used. For each sample, a series of spectra was recorded which were added together by means of a special procedure accounting the drift of the zero-time channel. The resultant spectra of very high statistics (at least  $3 \times 10^7$  counts) were obtained. Additionally, a reference spectrum for pure defect-free Si of statistics of  $10^8$  counts was collected which was used in order to determine the positron source contribution.

## Analysis

In the data analysis the LT-9-2 computer program was used [5, 6]. The program is able to perform simultaneous fitting of many spectra where the value of the model parameter can relate to a single spectrum (local parameter) or to all the spectra analyzed (common parameter). Besides, each parameter can be fixed at a required value or be free, i.e. to have an adjustable value. This way a model parameter can have one of the following four statuses: local free, common free, local fixed or local free. The division of parameters into the four groups is arbitral and can be set before starting the fitting procedure.

### A multi-exponential analysis

At the beginning, all the spectra of the investigated samples were analyzed simultaneously. Each spectrum was decomposed into four exponential components. First component (the so-called sample component) was assigned to positron annihilations in the examined material, the rest of components (called source components) related to annihilations inside the positron source and its covers. The sample component was described by a lifetime parameter of the local free status.

The lifetimes assigned to the source components were common and fixed at 125 ps, 387 ps and 2.06 ns (these values had been previously determined basing on the reference spectrum of Si). The source total contribution and relative contributions of the source components were set as common free. The goal of this analysis was to determine the positron average lifetimes in the investigated samples (the average lifetimes will be presented in the next section) and simultaneously the source contribution. The determined value of the total contribution of the source was 36.8%, which was constituted by 3 components in the following proportions 95.7% (125 ps), 3.6% (387 ps) and 0.65% (2.06 ns).

### Analysis with the two-state trapping model

Next, a part of spectra (see next section) were analyzed with help of the two-state simple trapping model (STM) in a form given in Ref. [6]. The model is implemented directly to the code of LT-9-2 software and can be selected as a calculation option.

The shape function of lifetime spectrum:

$$(1) \quad S^{\text{STM}}(t) = \lambda_f \exp[-(\lambda_f + \kappa)t] + \lambda_v \frac{\kappa}{\lambda_f + \kappa - \lambda_v} \cdot \{\exp(-\lambda_v t) - \exp[-(\lambda_f + \kappa)t]\}$$

is expressed by parameters of direct physical meaning, i.e.  $\lambda_f^{-1} = \tau_f$  is the lifetime of free positron,  $\lambda_v^{-1} = \tau_v$  is the lifetime of positron trapped by defects and  $\kappa$  is the positron trapping rate.

The spectrum analysis with the STM model in the form given by Eq. (1) has some advantages in comparison to the usually used analysis consisting in the decomposition of spectrum into two exponentially-shaped components:

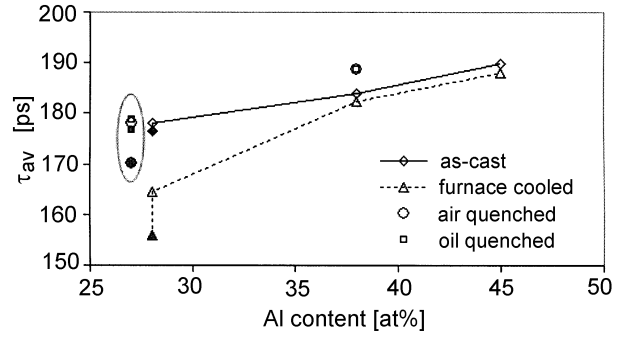
- The determined parameters have direct physical meaning, so no additional recalculations are required.
- When the analysis is performed simultaneously for  $n$  spectra, and  $\tau_f$  possesses the status of common free (or common fixed) then the number of free model parameters is reduced by  $n - 1$  (or by  $n$ ).

## Results and discussion

### The average positron lifetimes

The average positron lifetimes ( $\tau_{av}$ ) related to samples of different Al content and heat treatment are shown in Fig. 2. In general,  $\tau_{av}$  increases with increasing Al content. This tendency is in good agreement with the results reported by Diego *et al.* [1] although the respective absolute values of  $\tau_{av}$  measured by the authors are systematically a bit higher.

For the spectra of our Fe38Al and Fe45Al samples, one component approximation was sufficient for a perfect description of the experimental data. This also agrees with the results of Ref. [1] where for alloys of Al content close and higher than 40 at.%, quenched or cooled with furnace, only one lifetime component was observed. This fact can be explained by saturated trap-



**Fig. 2.** The average positron lifetimes for samples of FeXAl,  $X = 28, 38$  or  $45$  at.% (empty symbols) and Fe28Al5Cr (full symbols) after different heat treatment. The error bars are included into the symbols. For the sake of clarity, the indicated points related to Fe28Al and Fe28Al5Cr quenched to oil or air are shifted by 1 unit to the left.

ping of positrons in vacancy-type defects of concentration much higher than  $10^{-4}$ .

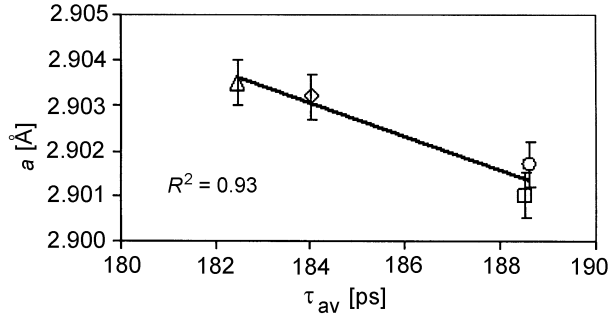
As shown in Fig. 2, the values of  $\tau_{av}$  in the Fe38Al samples quenched to oil or air are about 5 ps longer than in the sample cooled with furnace. The dependency of  $\tau_{av}$  on the cooling rate from high temperature was observed also by Diego *et al.* [1] for samples of Al content  $\geq 40$  at.%. The average lifetimes in samples quenched from  $1000^\circ\text{C}$  were higher than  $\tau_{av}$  in samples of the same composition, but slowly cooled from the same temperature. The authors assigned the effect to positron annihilations in different modifications of B2 structure present in the samples after fast or slow cooling. According to the phase diagram [8], quenched samples should retain a high temperature structure B2(h), whereas slowly cooled samples should have a low temperature B2(l) structure. Diego *et al.* [1] comparing the experimentally obtained  $\tau_{av}$  with theoretically calculated lifetimes in different types of defects speculated that in the B2(h) structure positrons are trapped mainly by triple defects (one anti-side Fe atom and two Fe vacancies separated by a lattice parameter), whereas in the B2(l) structure the dominant traps are Fe monovacancies.

Also XRD measurements carried out by us for the Fe38Al samples undergone different heat treatments seem to confirm the existence of the high and low temperature modifications of B2 structure as the lattice parameter  $a$  determined from the XRD patterns depended on the rate of cooling from high temperature (Table 2). We found quite a good correlation between  $a$  and respective  $\tau_{av}$  obtained for the Fe38Al samples (Fig. 3). This correlation suggests that the different values of  $a$  are caused by different types of defects in B2(h) and B2(l) structures.

In the case of samples of the lowest Al content,  $\tau_{av}$  depends strongly on the heat treatment (Fig. 2). Values of  $\tau_{av}$  for as-cast samples and quenched samples are

**Table 2.** The lattice parameter in the Fe38Al samples: in the as-cast state, heated at  $1000^\circ\text{C}$  for 48 h and next slowly cooled with furnace, quenched to oil and quenched to air

Sample	$a$ (Å) fur.-C	$a$ (Å) oil-Q	$a$ (Å) air-Q	$a$ (Å) as-cast
Fe38Al	2.9035	2.9010	2.9017	2.9032



**Fig. 3.** A correlation between average positron lifetime  $\tau_{av}$  and lattice parameter  $a$  in the investigated Fe38Al samples: as-cast (diamond), furnace cooled (triangle), air quenched (circle) and oil quenched (square).

much higher than the respective values for the furnace cooled samples. This tendency is especially visible for the samples in which 5 at.% of iron is substituted by chromium (full symbols in Fig. 2). This indicates that in the furnace cooling Fe28Al and Fe28Al5Cr samples, the concentration of defects is lowered to such a level at which a certain number of positrons can annihilate in the bulk material.

For the purpose of quantitative examining of the dependence between the cooling rate and the defect concentration in the samples containing 28 at.% Al, the lifetime spectra of these samples were analyzed once again with the help of the two-state simple trapping model (Eq. (1)).

#### Results of the two-state trapping model analysis

In this case the spectra of the Fe28Al and Fe28Al5Cr samples after oil quenching, air quenching and furnace cooling were analyzed. During the analysis, all the parameters describing the source components were fixed at values determined from the previous analysis. To reduce the number of free parameters we assumed that  $\tau_f$  depends on the sample composition but not on its heat treatment. Therefore, the spectra related to all the Fe28Al samples undergoing various heat treatment were fitted simultaneously with the common free status of  $\tau_f$ . A similar way of analysis was applied to the spectra of all the Fe28Al5Cr samples. In both cases,  $\kappa$  and  $\tau_V$  were treated as local free. The obtained values of  $\tau_f$  and  $\tau_V$  are shown in Table 3. The free annihilation lifetimes are much longer than the theoretical value ( $\sim 110$  ps) [1, 3, 9] expected for FeAl of D0<sub>3</sub> or B2 structures. They are also higher than the experimental value (112 ps) obtained for Fe<sub>3</sub>Al by Schaefer *et al.* [11]. However, the results are close to  $\tau_f$  determined by Jirásková *et al.* [3] (126.7 ps) for water quenched Fe<sub>72</sub>Al<sub>28</sub> and also to our previous measurement ( $\tau_f = 123$  ps) [7] for quenched Fe28Al samples. It is worth mentioning, that even for Fe<sub>3</sub>Al sample aged by one month at 410°C the average lifetime obtained was 125 ps [1]. These facts imply, according to literature suggestions [1, 3], that the usually determined  $\tau_f$  is really a resultant of the bulk lifetime and a lifetime in some types of defects (e.g. shallow traps where electron density is lower than in the bulk).

The comparison of the experimental values of  $\tau_V$  shown in Table 3 with theoretical predictions [1, 3, 9] allows to assign the lifetimes to various defects of

**Table 3.** The determined values of the positron bulk lifetime  $\tau_f$  (it was assumed independent of the samples heat treatment) and the lifetime  $\tau_V$  of positron trapped by defects in the samples undergone various heat treatment

Sample	$\tau_f$ (ps)	$\tau_V$ (ps)		
		Furnace cooled	Air quenched	Oil quenched
Fe28Al	124(1)	174(1)	180(1)	179(1)
Fe28Al5Cr	118(1)	170(1)	173(1)	178(1)

vacancy-type. The most probably  $\tau_V$  represents an average value of positron lifetimes in these defects. For fast cooled samples,  $\tau_V$  should mainly relate to positron annihilations in vacancies in Fe sublattice of the retained B2 ordered structure [1]. After slower cooling the dominant kind of defects seems to change, since  $\tau_V$  have a tendency to shortening. In slowly cooled samples one can expect forming of precipitates of the minor alloying elements (Table 1). According to our previous suggestion [7], the lowering of lifetimes may be connected with positrons annihilating in vacancies generated at these precipitates.

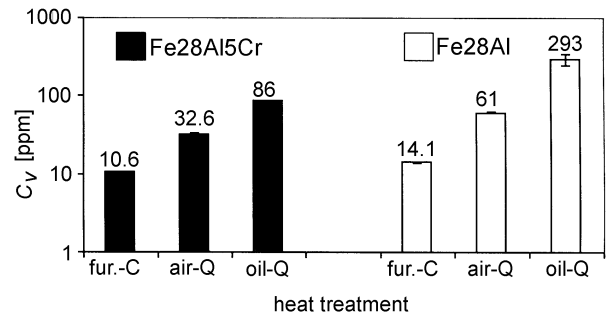
Figure 4 shows the estimated values of  $c_V$  in studied Fe28Al and Fe28Al5Cr samples as a function of their heat treatment. The concentration  $c_V$  is proportional to the positron trapping rate:

$$(2) \quad c_V = \kappa / \mu$$

The values of  $\kappa$  were taken from the fitting with STM model.

In our case we probably deal with a mixture of defects of different types and therefore of different trapping constants  $\mu$ . Therefore, both  $\kappa$  as well as  $\mu$  in Eq. (2), should be treated as effective quantities averaged over different trapping processes. Moreover, the absolute values of  $\mu$  are known for few kinds of defects only and with low accuracy, so the exact determination of  $c_V$  is a very difficult task. In our calculations we decided to use the same value of trapping constant ( $\mu = 2.5 \times 10^{14} \text{ s}^{-1}$  [11]), regardless of a sample composition and its heat treatment. Therefore, the determined absolute values of  $c_V$  should be treated only as roughly estimations, nevertheless, we hope that  $c_V$  ratios described the relative changes of defect concentrations quite well.

Figure 4 shows a strong dependence of  $c_V$  on the rate of cooling. It is worth underlining that the chromium addition reduces the concentration of resistance vacancies. This is especially pronounced in the oil quenched



**Fig. 4.** The estimated values of defect concentration in the Fe28Al5Cr and Fe28Al samples undergone various heat treatment.

samples. In the case of furnace cooled samples it is not so large. We observed a similar tendency in another measurement [7] carried out for samples of the same composition.

## Conclusions

The concentration of quenched-in vacancies increases with increasing Al content. When Al content is  $\geq 38$  at.%, the vacancy concentration is much higher than  $10^{-4}$ . Its absolute value cannot be determined by positron lifetime measurement because of saturated trapping of positrons.

The difference in the determined values of positron lifetimes for Fe38Al samples after quenching and slow cooling indicates the existing of the high temperature B2(h) and low temperature B2(l) modifications of B2 structure which differ in the lattice parameter and the type of dominant defects.

A very distinct dependence of retained vacancy concentration on the rate of cooling is shown for the investigated samples of 28 at.% Al. In quenched samples the concentration is of the order of  $10^{-4}$ , whereas in samples slowly cooled it is reduced to  $10^{-5}$ .

A strong influence of chromium addition on retained vacancy concentration is observed. The vacancy concentration in Fe28Al5Cr is lower than in Fe28Al if the materials underwent the same heat treatment.

**Acknowledgment.** This work was supported by the Ministry of Science and Higher Education of Poland under the grant 3T08A02430.

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